INSTITUTE NOTES.

DECEMBER, 1940.

MEMBERS SERVING WITH H.M. FORCES.

Corrections and additions to the first list of members serving with H.M. Forces, published in the October *Journal*, are given below. The Secretary will be pleased to receive additional information from time to time.

Adlington, R. E., promoted Major, R.A.
Rowntree, W. B., promoted Major, R.A.S.C.

Brooking, M., Flying-Officer, R.A.F.
Caplan, B., R.A.F.
Ellis, D. W. V., Lieut., S.A.E.C.
Evans, F. N. S., Lieut., R.A.S.C.
Newton, E. J., Sergeant, R.C.Sig.
van Sickle, R. K., Major, R.E.
Watling, R. A., Corporal, R.E.

AWARD OF SCHOLARSHIP.

The Institute scholarship of £40 per annum, tenable at the University of Birmingham, has been awarded to ALAN HENRY BALDWIN, Stud. Inst. Pet., at present studying in the Department of Oil Engineering and Refining.

ARTHUR W. EASTLAKE,
Honorary Secretary.

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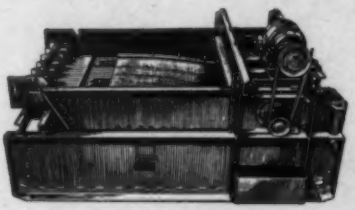

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Vol. 26. No. 206. December 1940.

FURTHER INVESTIGATIONS OF THE PROPERTIES OF CLAY SUSPENSIONS.*

By G. D. Hobson, Ph.D., D.I.C., A.M.Inst.Pet.

Summary.

A number of clay suspensions have been examined in a capillary tube viscometer under different pressure gradients. Data were obtained on the relationships between rate of flow and pressure gradient, concentration and "viscosity," simple and complex suspensions, and on the effects of heating, "viscosity"-temperature coefficients and ageing.

The Hatschek concentric cylinder viscometer did not prove very satisfactory for examining these suspensions. The phenomenon of sedimentation under shear in a concentric cylinder viscometer was investigated.

Attempts to determine yield values directly by using cylinders and vanes in a torsion apparatus brought to light an interesting feature which is probably coupled with thixotropy.

Preliminary work on the estimation of the amount of water "bound" by different clays was undertaken, and apparently amounts up to 25% or more of the weight of the dry clay are held thus.

I. The Capillary Viscometer.

In an earlier publication [1] the results of viscometric measurements on suspensions of Stockolite and Aquagel were described. The same apparatus has been applied to examine a number of clays and shales, some of which have been used in drilling muds. Briefly, the viscometer was of the pipette type, with interchangeable capillaries, and employed suction to draw a known volume of mud into the measuring-bulb. The apparatus was simple and cheap to construct; it had no drainage error. On the other hand, a fairly large volume of mud was required (350 c.c.), and working losses occurred when the bulb was cleaned between the observations. These losses increased with increasing "viscosity" of the mud. There was an upper limit to the pressure gradient which could be applied when using a given capillary. The presence of a hydrostatic-head correction and probable errors in the form used fixed a lower limit to the pressure gradient which could reasonably be applied with a given capillary. This correction was an approximate one for a true liquid, and therefore probably rather less satisfactory for muds. Kinetic-energy corrections were applied to the data. Little is known about the value of the coefficient m of the kinetic-energy correction in the case of these anomalous fluids, but it seemed preferable to use an approximate form rather than to omit the correction. It was possible to shake or stir the mud almost immediately before a measurement. This was of service when the clay suspensions sedimented relatively quickly. The muds could be stirred during an observation, thus providing a simple test for thixotropy.

If Cunningham's work [2] really showed that small differences in pressure affected the "viscosity," and not merely thixotropic effects, as suggested

* The greater part of the first two sections is summarized from a thesis approved for the Degree of Doctor of Philosophy in the University of London, 1936.

by McMillen,[3] and the effect does not reach its maximum instantaneously or in a few seconds at the most, it cannot appreciably affect the results in this apparatus; for the mud is kept under the same pressure right up to the moment of entering the capillary, whatever the pressure gradient used. It is clear, as Ambrose and Loomis,[4] and McMillen [5] point out, that if a thixotropic material does not attain equilibrium in a concentric cylinder rotating viscometer in 30 minutes, or more in some instances, it will scarcely be possible to reach equilibrium in a capillary of the usual length. Yet if a long period of shearing is necessary for the attainment of this equilibrium, the possibility exists that the thixotropic state during the passage through the capillary will not be far removed from that obtaining immediately before entering the capillary.

All the muds were made up with distilled water, the shales and clays being crushed where necessary, and they were screened to pass 60-mesh I.M.M. The concentrations have been expressed as the percentages by weight of the clays in the suspensions, and were determined by heating weighed samples to dryness at 110° C. Unless otherwise stated, the measurements were made at 20° C. The capillaries had the following dimensions :—

I N. Length : 11·580 cm
Radius : 0·0434 cm.

II N. Length : 11·361 cm.
Radius : 0·0432 cm.

I W. Length : 11·644 cm.
Radius : 0·0638 cm.

The data have been interpreted in two ways :—

(*a*) From the corrected pressure gradient and the time of filling of the bulb, the equivalent or apparent viscosity was calculated as that of a hypothetical normal liquid according to the following equation :—

$$\eta_{is} = \frac{\pi P R^4}{8V(L+nR)} - \frac{mV\rho}{8\pi(L+nR)}$$

where R and L are the radius and length of the capillary respectively, ρ is the density of the mud, $V = \dfrac{\text{measuring volume of viscometer}}{\text{time of filling}}$, m is the coefficient of the kinetic-energy correction, n the coefficient of the Couette end-correction, and P is the corrected pressure. The equivalent viscosity calculated for each observation was plotted against the corresponding mean rate of flow. The method is empirical. Nevertheless it is of service.

(*b*) The quantity $\dfrac{V}{\pi R^3}$ was plotted against $\dfrac{PR}{2L}$, after applying a kinetic-energy correction to the pressure gradient.

Since the rate of flow changed a little in each observation and the hydrostatic and kinetic-energy corrections were but approximate, it is to the relative, and not the absolute, values of the results that the chief attention must be paid. The equivalent viscosities have been expressed in terms of poises in order to give some idea of the magnitudes of the quantities involved.

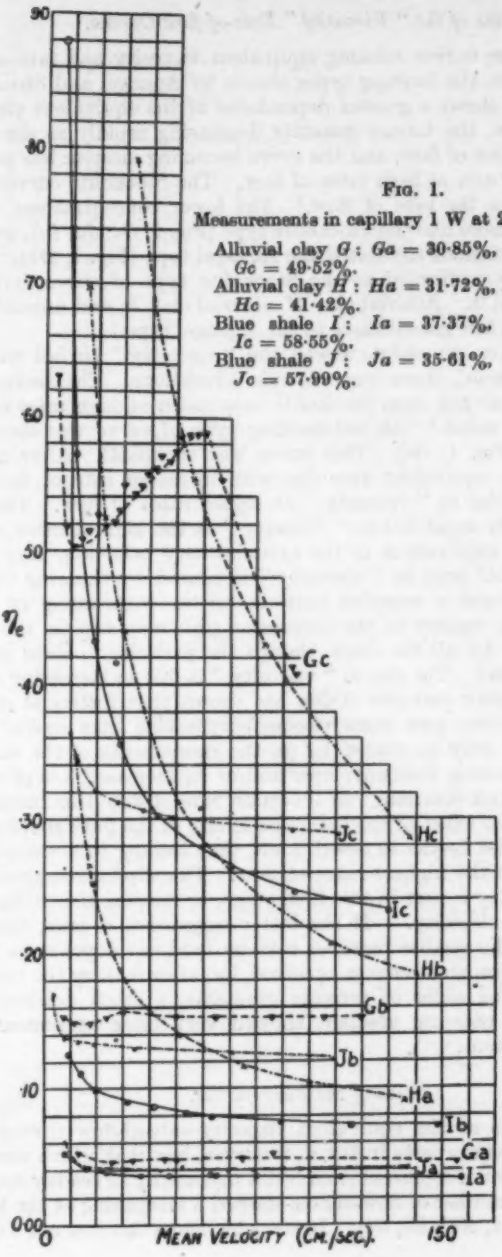


FIG. 1.

Measurements in capillary 1 W at 20° C.:—

Alluvial clay *G*: *Ga* = 30·85%, *Gb* = 42·70%, *Gc* = 49·52%.
Alluvial clay *H*: *Ha* = 31·72%, *Hb* = 37·65%, *Hc* = 41·42%.
Blue shale *I*: *Ia* = 37·37%, *Ib* = 49·16%, *Ic* = 58·55%.
Blue shale *J*: *Ja* = 35·61%, *Jb* = 51·11%, *Jc* = 57·99%.

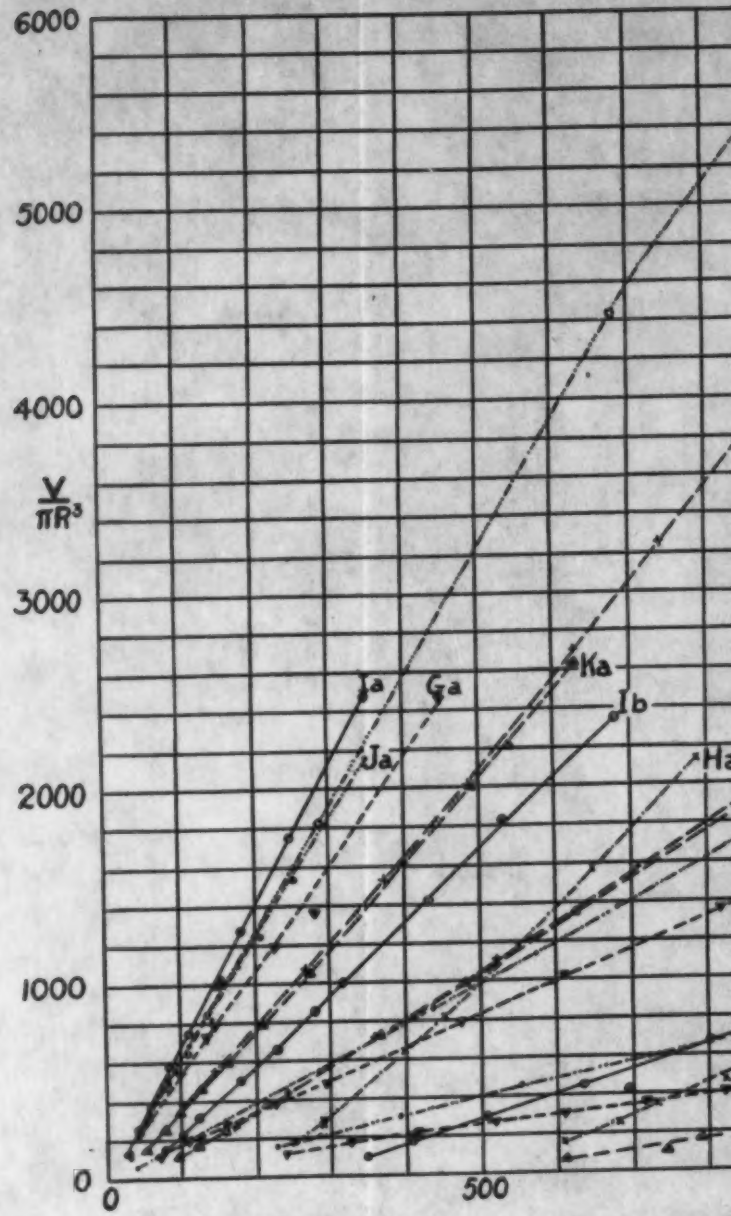
Forms of the "Viscosity" Rate-of-flow Curves.

The forms of the curves relating equivalent viscosity and rate of flow seem to lie between the limiting types shown by Aquagel and Stockolite. The Aquagel type shows a greater dependence of the equivalent viscosity on the rate of flow, the former quantity decreasing rapidly as the latter increases at low rates of flow, and the curve becoming more or less parallel to the rate-of-flow axis at high rates of flow. The Stockolite curves show less dependence on the rate of flow.[1] The lower concentrations of the clays gave curves more like the Stockolite type (Fig. 1, *Ga*, *Ja*, *Ia*), whereas the higher concentrations simulated the Aquagel type (Fig. 1, *Hb*). None of the clays quite conformed to the Stockolite type of curve, but blue shale *J* approached it. Alluvial clay *H*, alluvial clay *R*, and unweathered London clay had a fair resemblance to the Aquagel type.

Whilst the curves generally showed the "viscosity" to fall with increased rate of shear, there were certain exceptions. The increase in "viscosity" of a 40 per cent. Stockolite suspension at high rates of flow has already been noted.[1] An outstanding type of curve was shown by alluvial clay *G* (Fig. 1, *Gc*). This curve was sigmoidal. After a very rapid decrease in equivalent viscosity with increased rate of flow, the curve revealed a rise in "viscosity" at higher rates of flow. This was followed by a fairly rapid fall in "viscosity" at the highest rates of flow used. A possible explanation of the extraordinary behaviour may be as follows: The initial drop in "viscosity" is caused by shearing off of a fluid envelope around a complex particle, or the overcoming of forces which tend to give rigidity to the suspension (this may explain the "viscosity" reduction for all the clays, though the particles in them are not necessarily complex). The rise in "viscosity" is due to increasing breakdown of the complex particles (Oden has shown that for equal concentrations, fine particles give more viscous suspensions than coarse ones). In detail, the rise may be caused by (*a*) the components of the complex particles each assuming fluid envelopes and/or (*b*) increased loss of energy due to collisions and rotation. At a certain rate of flow this breakdown is complete, and the effect of the reduction in size of the fluid envelopes on the smaller particles begins to assert itself, thus leading to a second drop in "viscosity" at the highest rates of flow. The slippage suggested by Bingham [6] may play a part in this final stage, or may be the entire cause of the drop in "viscosity." If the latter suggestion is true, then the assumption that the smaller particles take on fluid envelopes is no longer necessary. No permanent change occurred, for, after making the measurements in decreasing order of pressure gradients, a check determination under the initial pressure gradient showed very close agreement with the first measurement.

Form of the Flow-curves.

The peculiarities of the equivalent viscosity–rate-of-flow curves have, of course, their counterparts in the flow-curves, but that which shows up well in the one form of representation is not necessarily so readily apparent in the other. A number of flow-curves showed a steepening at the highest rates of flow (Fig. 2, *Kb'*, *Hc*, *Gc*). In some instances this was not a change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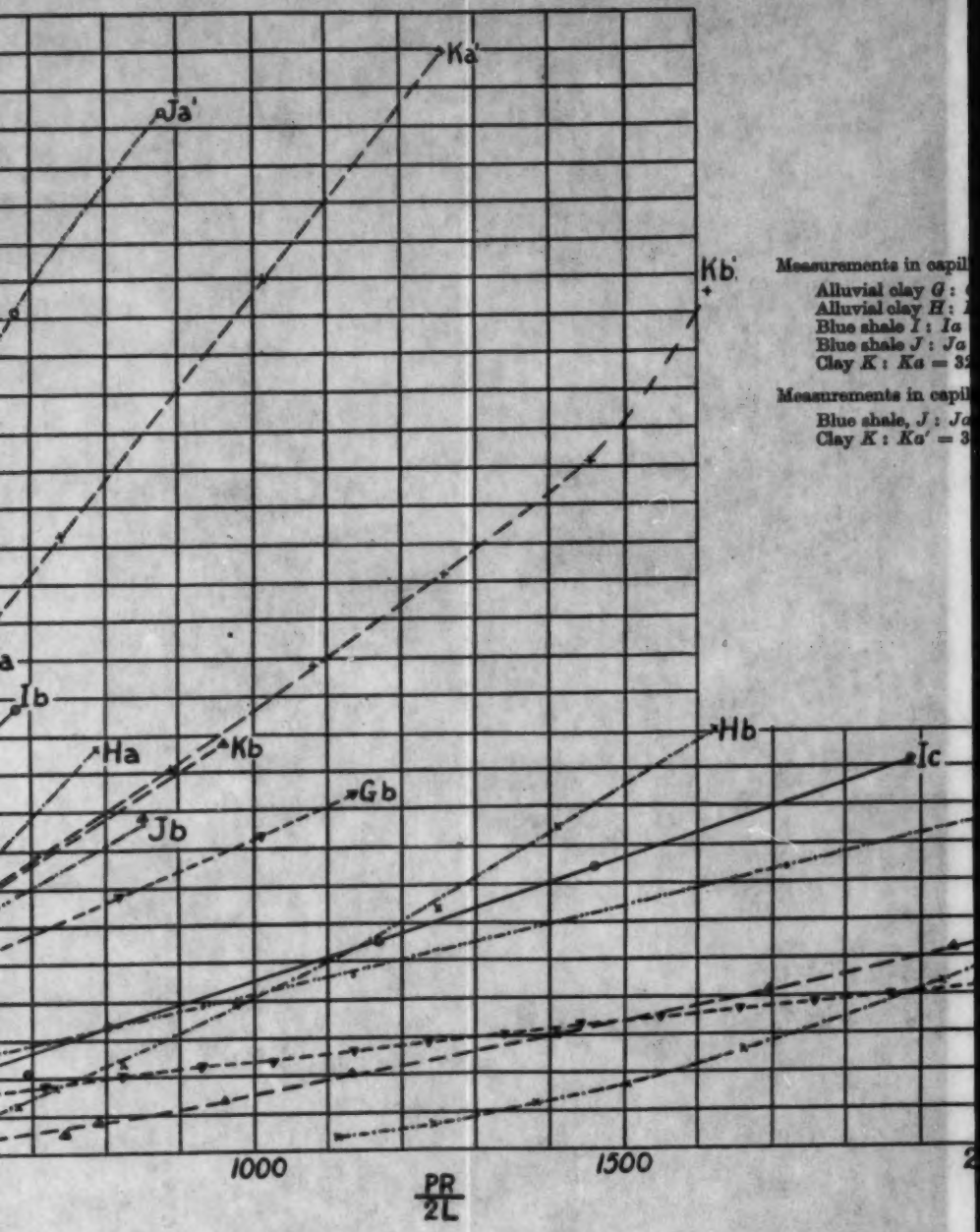
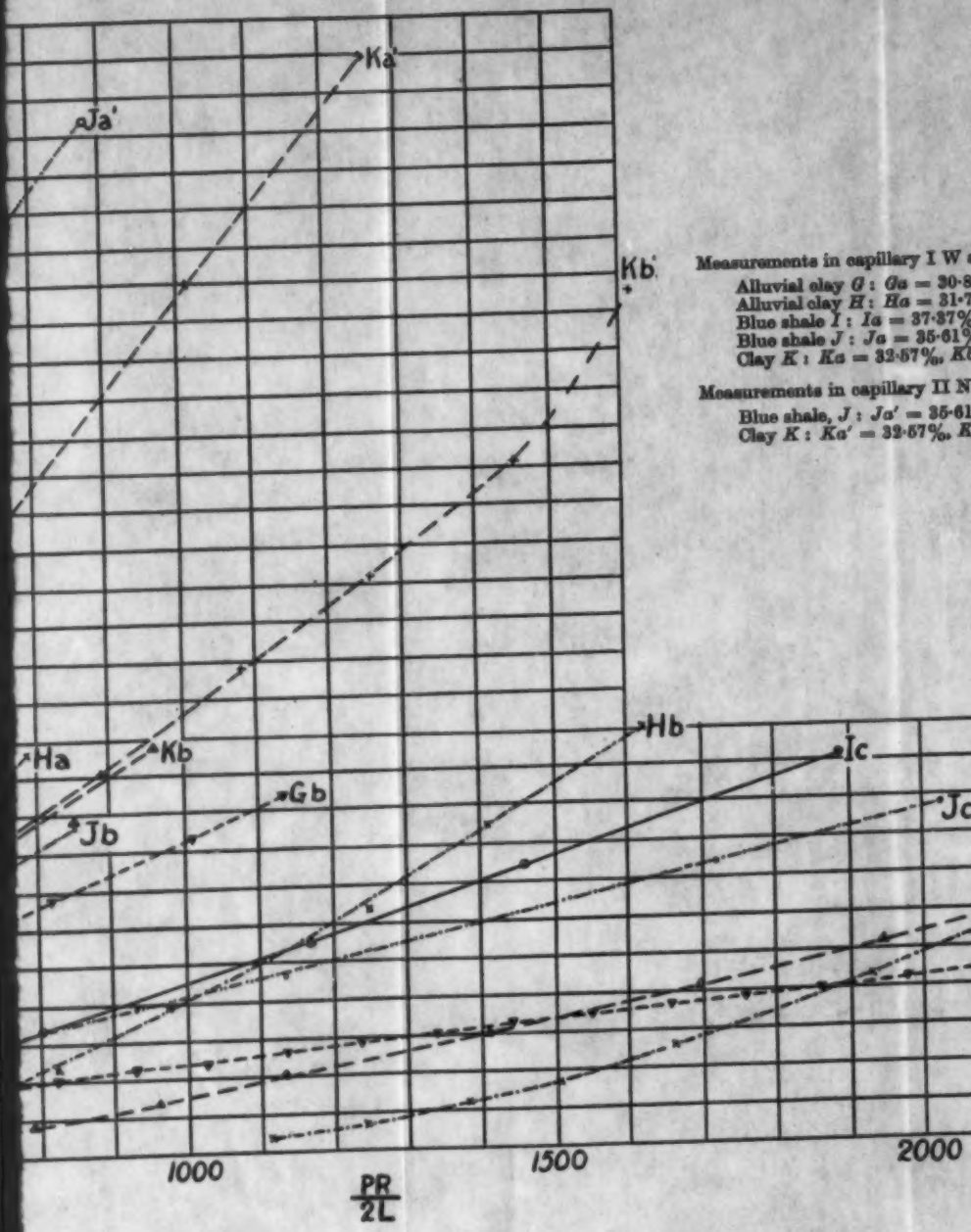


Measurements in capil
Alluvial clay G :
Alluvial clay H :
Blue shale I : Ia
Blue shale J : Ja
Clay K : Ka = 32
Measurements in capil
Blue shale, J : Ja
Clay K : Ka' = 3

FIG. 2.



Measurements in capillary I W

Alluvial clay G : Ga = 30·8

Alluvial clay H : Ha = 31·7

Blue shale I : Ia = 37·37%

Blue shale J : Ja = 35·61%

Clay K : Ka = 32·57%, Kb

Measurements in capillary II N

Blue shale, J : Ja' = 35·61

Clay K : Ka' = 32·57%, K

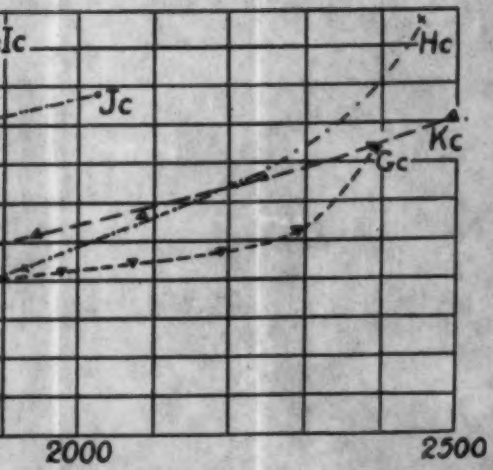
FIG. 2.

n capillary I W at 20° C. :—

y G : Ga = 30·85%, Gb = 42·70%, Gc = 49·52%.
y H : Ha = 31·72%, Hb = 37·65%, Hc = 41·42%.
I : Ia = 37·37%, Ib = 49·16%, Ic = 58·55%.
J : Ja = 35·61%, Jb = 51·11%, Jc = 57·99%.
a = 32·57%, Kb = 39·91%, Kc = 46·41%.

n capillary II N at 20° C. :—

J : Ja' = 35·61%.
a' = 32·57%, Kb' = 39·91%.



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in mobility, but was at least partly due to air coming out of solution. The cases of a true increase in mobility were possibly examples of slippage or loss of fluid envelopes. In other instances the flow-curves became less steep at the highest rates of flow (Fig. 2, *Ja'*). This probably resulted from turbulence, with the possible additional factor of breakdown of complex particles.

Although some of the flow-curves were still straight at the lowest rates of flow used, many of them did show curvature towards the origin. The Bingham hypothesis demands such curvature even though slip be absent, and if slip be present, the curvature is greater, and the curve may even pass through the origin, as Buckingham assumed in the derivation of his equation, or may intersect the stress axis at a measurable value, as observed by Keen, Scott Blair, and Crowther.[7, 8]

Whilst the flow-curves of blue shale *L*, shale *P*, and clay *K* were essentially straight lines, except at the lowest rates of flow, some of the other clays, and especially the higher concentrations, gave flow-curves which curved throughout, with the result that a reasonable measurement of their slopes was difficult or impossible.

In conformity with the observations of Hall,[9] and Scott Blair and Crowther,[8] it was found that the slope of the part of the flow-curves corresponding to stage IV of the latters' curves was greater the narrower the capillary—*i.e.*, the mobility was higher in the narrow capillary.

Effect of Stirring, etc., on the Measurements.

In the bulk of the measurements the standard procedure was to stir the mud for 25 sec. immediately before the measurement, and at a steady rate during the measurement. This stirring was by no means vigorous, but it was found possible in most cases to obtain more consistent results with stirring during the measurements than when stirring was suspended. The exceptions were some very dilute suspensions of fractions of London clay and there, no doubt, the irregularities were due to turbulence.

Omitting the cases of fractions of London clay, stirring during a measurement was found to give a lower value for the "viscosity" or a higher value for the mobility than was observed in the absence of stirring. Thus stirring increased the mobility of a Stockolite–Aquagel suspension by about 10 per cent.

Any disturbance might be expected to tend to promote turbulent flow. Such a tendency would be greater the more vigorous the stirring, and for a fixed method of stirring it would be greater the less dense and the less viscous the fluid. If the fluid were thixotropic, the nett effect of stirring during a measurement would be manifest as an increase or decrease in the "viscosity," according as the apparent increase in "viscosity" resulting from any turbulence created exceeded or was less than any decrease in "viscosity" consequent on thixotropic breakdown.

It must be recognized that if any standard method of treatment is adopted with a thixotropic mud—*e.g.*, stirring during an observation, not stirring, or stirring vigorously before an observation—then, provided that the measurements are made in strict order of increasing or decreasing pressure gradients, the results may be expected to lie on a smooth curve,

but the curve obtained for the increasing order of pressure gradients will not necessarily coincide with that obtained for the reverse order. The reason lies in the fact that the treatment, whatever its nature, will only in rare cases maintain the initial state of thixotropic breakdown during a series of measurements. In general it will either fail to maintain it, or it will increase it. Notwithstanding, under uniform treatment the change in thixotropic state may be expected to be gradual, and hence a smooth curve will result. On this account, mobilities and stress intercepts may differ a little according as observations are made in ascending or descending order of pressure gradients.

Relationships between Concentration and the " Viscosity " or Mobility of the Suspensions.

Although the " viscosities " at given rates of flow can be plotted against the concentration by weight, in attempts to find a relationship between " viscosity " and concentration, it is desirable to use a less arbitrary quantity, *e.g.*, the ultimate viscosity—the asymptotic value towards which the " viscosity "–rate-of-flow curves seem to tend in most cases—or the value, *i.e.*, the mobility, obtained from the slope of the flow-curves in stage IV when they are linear or nearly so. The reciprocal of the mobility has the dimensions of a viscosity. Furthermore, it would seem better to express the concentration in terms of volume rather than weight, for it is the size of the particles and their total effective bulk which, other things being equal, determine the " viscosity " of a suspension, and it is clear that the relationship between percentage by volume and percentage by weight is not linear unless the densities of the suspended material and the suspending medium are equal. There is an additional complicating feature in that the particles are probably intimately associated with a portion of the suspending medium, making their effective bulk appreciably greater than that of the particles alone. However, this feature has been omitted from the following simple discussion.

In order to calculate the concentration by volume from that by weight in the absence of direct determinations of the densities of the clay particles, a density value of 2·6 was used, which, while somewhat below a series of computed apparent densities, probably errs in the right direction.

Einstein's equation for the " viscosity " of a suspension of rigid spheres is $\eta_s = \eta(1 + 2{\cdot}5\phi)$, where ϕ is the volume fraction the spheres constitute of the entire suspension. This equation assumes that the spheres do not influence one another. The suspensions examined do not obey this linear relationship, but the " viscosity " increased at a greater rate, a result to be expected from the high concentrations used (Fig. 3). In addition, the particles were most likely platy, and may not have fulfilled the condition of rigidity. Bingham and Durham's work on infusorial earth and English china-clay led them to the conclusion that finely divided substances in suspension depress the fluidity $\left(\frac{1}{\text{viscosity}}\right)$ of the liquids in which they are suspended by amounts which are directly proportional to the volume of solid.[11] This may be expressed by the equation $\phi_s = \phi_w\,(1 - \phi k)$, where ϕ is the volume fraction of the solid.

The percentage by volume has been plotted against the mobility (Fig, 4). In no case was a straight line obtained. Nevertheless, the curvature was not great. Aquagel was found to approximate more closely to Einstein's equation than to Bingham and Durham's, whereas Stockolite and the other clays were, on the whole, nearer to Bingham and Durham's. The closer agreement of Aquagel with Einstein's equation was perhaps to be expected, since the maximum concentration was only 1·86 per cent., whilst the other suspensions went up to 35 per cent. of clay by volume.

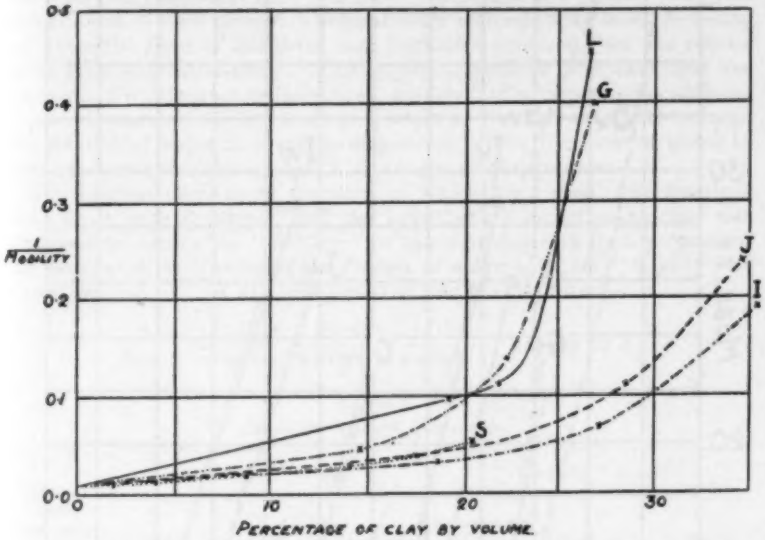


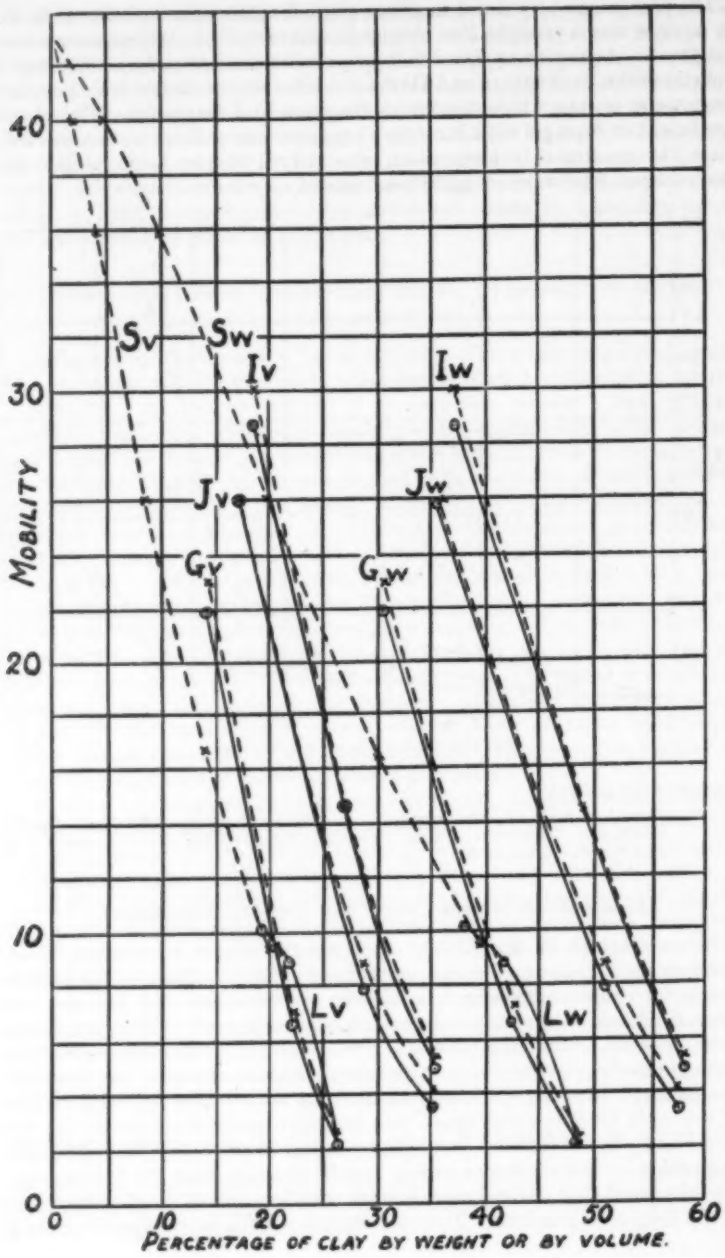
Fig. 3.

Measurements at 20° C.:—

G—alluvial clay *G*; *J*—blue shale *J*; *I*—blue shale *I*; *L*—blue shale *L*; *S*—Stockolite. Curves *G*, *J* and *I* are for capillary II N; *L* for capillary I W, and *S* for capillary I N.

Relationships between Simple and Complex Suspensions.

In an attempt to find if any approximate simple relationship exists between the " viscosity " or the mobility of composite suspensions and the values for simple suspensions, a mixture of Stockolite and Aquagel, and three fractions of unweathered London clay were used. The suspensions were made up so that the ratio of a given material or fraction to the total volume present was the same in the simple suspension as in the composite suspension. In using the above method the ratio of the effective volume of the solid to free-water space was not necessarily identical in the two cases, and when it differed, it would be higher in the case of the composite suspension—a circumstance which would indicate that its " viscosity " should exceed that derived merely from consideration of the " viscosities " of the simple suspensions. It would therefore have been more accurate to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PERCENTAGE OF CLAY BY WEIGHT OR BY VOLUME.

have made up the simple suspensions so that the ratio of the effective volume of solid to the volume of free water was the same as in the composite suspension, but lack of knowledge of the water-" binding " power of the various fractions precluded this.

The increments to the viscosity of water caused by the separate fractions or materials at given rates of flow were summed and added to the viscosity of water. The summate curve was found to lie well below that actually obtained for the composite suspension. This was not unexpected, for with every material the " viscosity " increased at a greater rate than the amount of solid present. Several other methods were tried, including an extended form of Bingham and Durham's equation, but the results were even less satisfactory. Finally, the hypothesis was used that the addition of a substance reduced the " fluidity " of a suspension containing a second substance, in the same proportion as the first substance reduced the fluidity of water in a simple suspension, where the ratio of water to that substance was the same as in the composite suspension.

For London clay, three fractions of which were used, two fractions were dealt with as above, and the hypothetical mixed suspension was supposed to reduce the " fluidity " of the third fraction by a proportion the same as it itself reduced the fluidity of water—*i.e.*, the " fluidity " of a mixture $A,B, \ldots X$ at a given rate of flow is as follows :—

$$\frac{\text{" fluidity " of } A}{\text{fluidity of water}} \cdot \frac{\text{" fluidity " of } B}{\text{fluidity of water}} \cdot \ldots \text{ fluidity of } X,$$

TABLE I.

Stockolite–Aquagel Suspension.

Rate of flow, cm./sec.	" Fluidity " (rhes).			" Viscosity " (poise).		
	Calc.	Obs.	% error.	Summation of visc. increm.	Observed.	% error.
30	15·6	16·3	−4·3	0·0442	0·0611	−27·9
60	17·9	18·1	−1·0	0·0408	0·0550	−26·0
90	19·2	19·2	0·0	0·0386	0·0520	−25·7
120	20·3	20·1	0·7	0·0371	0·0495	−25·0
150	21·1	20·9	1·6	0·0360	0·0480	−25·0
180	21·6	21·5	0·3	0·0353	0·0465	−24·0
210	21·9	22·0	−0·6	0·0347	0·0454	−23·3
240	21·6	22·7	−4·7	0·0337	0·0440	−21·0

all the data being for the same rate of flow, and the ratio of $A,B, \ldots X$ to water in the simple suspensions being the same as in the composite

FIG. 4.

v denotes curve for percentage by volume.
w " " weight.
G is alluvial clay *G*; *J* is blue shale *J*; *I* is blue shale *I*; *L* is blue shale *L*; *S* is Stockolite.

Full lines are for capillary I W; broken lines for capillary II N, except in the case of Stockolite where the results are for capillary I N. The ordinates of the Stockolite curves have been halved.

TABLE II.

Unweathered London Clay.

Rate of flow, cm./sec.	"Fluidity" (rhes).			"Viscosity" (poise).		
	Calc.	Obs.	% error.	Summation of visc. increm.	Observed.	% error.
15	1·92	3·1	−38·0	0·222	0·322	−31·0
30	4·15	4·6	− 9·9	0·147	0·216	−32·1
50	5·8	6·3	− 8·0	0·117	0·159	−26·1
80	7·2	7·6	− 5·2	0·096	0·132	−27·3
110	8·1	8·7	− 6·9	0·087	0·115	−24·2
140	8·84	9·3	− 4·9	0·082	0·108	−23·9
170	9·5	10·1	− 6·0	0·078	0·099	−21·0

suspension. In Tables I and II the results so obtained are compared with those reached from the summation of "viscosity" increments.

Tables I and II show that the results reached by the last method agree more closely with observed values than do the summations of viscosity increments. The large error for the lowest rate of flow in Table II is probably due to inaccuracies in the experimental data, for it is most difficult to make the measurements at the lowest rates of flow with certainty.

A natural extension to the above hypothesis is its application to the relationship between concentration and mobility for a single clay. This gives $\log \psi_s = \log \psi_w + \frac{99C}{1-C} \cdot \log a$, where C is the fraction by volume of solid in the suspension and a is the ratio of the mobility of a suspension with 1 per cent. by volume of solid to the fluidity of water. Moderate agreement with this equation was shown by the Stockolite data, and those for blue shale *I*. Alluvial clay *G* and blue shale *J* gave curves of a similar form, and the latter showed quite good agreement with the extended form of the equation which makes some allowance for "bound" water (Fig. 5).

Stress Intercept.

The intercept on the stress axis obtained by extrapolating the stream-line portion of the flow-curves has received a variety of names. It has been called the "static rigidity" by Keen.[12] Terzaghi [13] criticized this, and suggested "shearing resistance." Buckingham has used "shearing strength," and Bingham "yield value." The significant physical factor is the critical shearing stress required to initiate flow as assumed in the Bingham hypothesis. This is three-quarters of the stress intercept, and in spite of the general application of the various terms to the stress intercept, it would seem preferable to reserve them for the quantity which is considered in the general theory. For the present purpose "yield value" will be adopted, and taken as three-quarters of the stress intercept.

Where possible, extrapolation of the stream-line portion of the flow curves was carried out, and yield values were measured, ranging from zero up to several hundred dynes/sq. cm. The values varied widely for

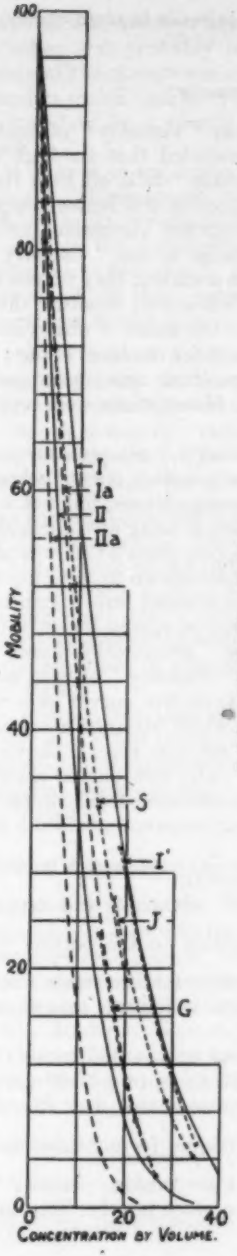

FIG. 5.

Curves I and II represent the equation $\psi_s = \psi_w a^{\frac{99\sigma}{1-\sigma}}$, where ψ_w is the fluidity of water at 20° C., and 'a' has the values of 0·95 and 0·90 respectively. Curves Ia and IIa represent the equation $\psi_s = \psi_w a^{\frac{99k\sigma}{1-k\sigma}}$, where k is the ratio of the effective volume of the suspended solid to its actual volume and is given a value of 1·5 here, and 'a' has values of 0·95 and 0·90 respectively. Curve G shows data for alluvial clay G; I' for blue shale I; J for blue shale J; S for Stockolite. Curves G, I', and J are for capillary II N, and curve S is for capillary I N.

the different clays, and increased rapidly with increase in concentration of the clay.

Effect of Heating the Suspensions.

As a result of a series of measurements of the "viscosity" of muds at different temperatures, Craft and Exner [14] concluded that for high concentrations and also for bentonites the "viscosity" falls off with rise in temperature up to about 60° C., and then increases at still higher temperatures. These observations were made in a Stormer viscometer using a constant driving-weight; consequently any change in the "viscosity" of this type of medium would be exaggerated. In addition, they do not state what precautions were taken against evaporation losses; whether the one sample was kept in the instrument throughout the series of observations; whether the concentration increased during the series of observations; and whether the "viscosity" at the initial temperature was unchanged by heating and the same curve was obtained if the observations were repeated in descending order of temperatures.

Preliminary attempts to determine a "viscosity"–temperature coefficient for these clay suspensions led to some peculiar results when the measurements were made in rising order of temperatures, but not so for measurements in the reverse order, the same sample being used throughout. It was clear, therefore, that some change was taking place which was unlike the mere fall in viscosity with rise in temperature shown by true liquids.

A 16·69 per cent. suspension of clay *N* was divided into a number of parts, each of which was heated to one of a series of temperatures, ranging from 20° C. to 99° C., for a period of 7 hours. Evaporation losses were prevented, and after standing over-night, the "viscosity" of each sample was measured at 20° C. The "viscosity" rate-of-flow curves as a whole showed there was an increase in "viscosity" which attained a maximum in the samples heated to 70–80° C., and for samples heated above that temperature range the "viscosity" fell off. The flow-curves showed a fairly distinct division into three parts, but the inferences from comparisons of corresponding parts were similar. The stress intercept attained a maximum over the range 60–80° C., whilst the $\frac{1}{\text{mobility}}$ showed a continuous increase up to the highest temperature used. Over the full range the $\frac{1}{\text{mobility}}$ increased by 14–18 per cent., according to the portion of the flow-curves considered, and the maximum values for the stress intercept were 34–52 per cent. higher than for the sample which was maintained at a temperature of 20° C.

A 32·94 per cent. suspension of the same clay was heated to 55° C. and the "viscosity" measurements compared with those of a 16·69 per cent. suspension similarly treated. The percentage increases in "viscosity", $\frac{1}{\text{mobility}}$, and stress intercept in terms of the values for unheated samples were much greater in the more concentrated suspension. Similar "viscosity" increases were observed to have taken place in other clay suspensions after heating to 40° C.

Tests on a suspension heated at 45° C. for varying periods showed that the change was probably complete after 6–10 hours. Finally, the permanence of the change was examined. For this purpose the 16·69 per cent. suspension which had been heated to 90° C. for 7 hours was re-examined after standing for a month. The results showed the change to be permanent.

It is clear that the hysteresis in the preliminary essays at measuring a "viscosity"–temperature coefficient was due to non-reversible changes which set in in previously unheated suspensions. It follows, therefore, that whether the "viscosity" will appear to increase or decrease as the temperature is first raised, will depend on the relative magnitudes of two factors which, in these cases, operate in opposite directions for the lower temperatures at any rate :—

(*a*) A normal decrease in "viscosity" (with rise in temperature) resulting from the decrease in viscosity of the suspending medium. This is reversed on reducing the temperature.

(*b*) A change in "viscosity" due to the heating which is not removed on lowering the temperature, and, as far as the present measurements go, is seemingly permanent.

This second factor will not appear in measurements made in descending order of temperatures, provided that the "viscosity" change has been allowed to attain its maximum at the highest temperature used. If that state has not been reached, the temperature coefficient may be exaggerated if heating raises the "viscosity." On the other hand, for observations made in rising order of temperatures on previously unheated suspensions, an apparently low or even negative value will be obtained in the presence of this factor.

The findings described seem to be at variance with those of the Burmah Oil Company,[15] but it may be that all clays do not behave alike. Yet, in the absence of information regarding the experimental details mentioned, the present work appears to offer a reasonable explanation of Craft and Exner's results.

Effect of Temperature on the Mobility and "Viscosity" of the Muds.

According to Hatschek,[16] the temperature coefficient of "viscosity" in suspensoid sols is merely that of the dispersion medium. In contrast, the temperature coefficient of emulsoid sols "is always markedly greater than that of the dispersion medium."

For 10 and 40 per cent. Stockolite suspensions the relative changes for the range 10–30° C. were slightly less than for water. The same was true of 20 per cent. Stockolite treated with 1·998 per cent. of caustic soda.

Two other clays were examined. Since their flow-curves were not linear in stage IV, but showed a small fairly uniform curvature, it was not possible to measure the $\frac{1}{\text{mobility}}$ in the usual manner. Consequently the data were compared empirically. The mean slopes of the curves for similar ranges of $\frac{V}{\pi R^3}$ (rates of shear) were measured, and from these the percentage

changes in $\frac{1}{\text{mobility}}$ for the intervals 40 — 20° C., 30 — 20° C., and 40 — 30° C. were obtained and compared with the values derived from the equivalent viscosity–rate-of-flow curves and the viscosity changes for water. The changes calculated from the flow-curves approached more closely to those for water than did those obtained from the "viscosity" curves. In the former case, for a 59·91 per cent. blue shale *I* suspension the agreement was within a little more than 1 per cent., whilst for the 40·65 per cent. clay *K* suspension, which was probably more colloidal, the mean change was about 4 per cent. less than for water.

A 37·63 per cent. suspension of clay *N* had a $\frac{1}{\text{mobility}}$ at 55° C. which was 46 per cent. of its value at 20° C. The viscosity of water at 55° C. is 50 per cent. of its value at 20° C. Hence the change was slightly greater than that for water.

A sound opinion as to the effect of rise in temperature on the stress intercept cannot be given from the present data, for the flow-curves not being linear in stage IV rendered extrapolation unreliable.

Ageing.

Hall [9] found that "the consistency of a clay slip changes during the first two days, probably due to the swelling of gel colloids, and more on the first day than in later periods. All the determinations with one capillary must be made in one day due to the time effect on the consistency of the slip." Excepting the cases of the Stockolite suspensions, the "viscosity" measurements here described have not been made on the day on which the suspensions were prepared, and in only three instances—38·28 per cent. blue shale *L*, 51·11 per cent. blue shale *J*, and an Aquagel suspension—were measurements carried out on the first day after preparation. Naturally flow-curves were drawn only for data obtained on the same day.

Stockolite suspensions of concentrations 20, 30, and 40 per cent. were examined on the day of preparation and again after intervals of 35 days, 31 days, and 8 days, respectively, but no indication was found of any change in "viscosity" with age.

The increased effect of caustic soda and hydrochloric acid on Stockolite as compared with measurements made within a short time of adding the reagent has been noted.[1] For soda-treated Aquagel small irregularities in the curves frequently coincided with over-night intervals.

The suspension consisting of a mixture of 20 per cent. Stockolite and 2·925 per cent. Aquagel showed a very strong increase in "viscosity" or decrease in mobility with age. Comparing measurements made within a day or two of its preparation with those made nine months later, the latter revealed a "viscosity" increase of about 40 per cent. for observations under similar conditions, and examination of the flow-curves showed that not only had the mobility decreased, but the stress intercept had increased by 37·5 per cent. This suspension "set" slowly to a gelatinous mass with well-marked solid and elastic properties, yet a few moments' shaking converted it into the original liquid with no signs of any "solid" lumps.

Some clay suspensions showed no important differences in mobility

between being a few days and several months old, whilst others showed considerable differences between being two or three days and ten days to several months old.

It is possible that the " viscosity " increases are concomitant with slight volumetric contractions, for a small increase in density was noted in a suspension of clay *K* between being three days and seven weeks old.

Distribution of Particle Sizes, Surface Factors and Inferences from the Chemical Analyses of some of the Clays.

An attempt was made to determine the approximate size distribution of the particles in a few of the clays, and thus to arrive at an estimate of the relative total surface per gram of each clay, with a view to finding whether or not this factor gives a clue to the fluid and other properties of the suspensions. The pipette method of mechanical analysis was adopted, using a suspension containing about 2 per cent. by weight of solids in distilled water. (The suspensions were prepared by diluting those used for " viscosity " measurements, which were all several months old.)

The assumptions involved in the application of Stokes' law to the mechanical analysis of sediments are well known. The bulk of the particles in a clay will be platy rather than spherical, and their " effective radii " are the radii of imaginary spheres of the same material which would sink in water with the same velocities as the particles in question. The specific gravities of the particles probably vary a little, and there may be adsorption of the suspending medium.

Fig. 6 shows the cumulative curves from which the size-distribution curves were derived by graphical methods. Using graphical methods again, surface distribution curves were obtained, and thence the relative total surface per gram of each clay was estimated. In this estimation the assumption was made that the particles were spherical and of uniform specific gravity. The effective radii of the cumulative curve were employed. If the particles were laminar rather than spherical, their falling velocities might be assumed to be, on the average, considerably less than for spheres of the same weight. The normal method of using Stokes' law would mean that a single laminar particle would be represented as more than one small sphere. Thus, whilst a laminar particle has a greater surface than a sphere of equal weight, the fact that its lower falling velocity leads to its interpretation as more than one small sphere will give a total surface factor nearer the truth than the small spherical particle of equal weight. Furthermore, if there is a fair degree of geometrical similarity in the particles of the different clays, relative estimates will not be so seriously disturbed by using spheres as the basis for calculation.

Joseph [17] has emphasized the importance of the silica–sesquioxide ratio as a guide to the plasticity of clays. The higher this ratio the greater the degree of swelling and dispersibility, the more viscous the suspensions, the greater the heat of wetting, adsorption of basic dyes and base exchange,[18] the higher is the electrokinetic potential when containing a given cation, in the absence of added electrolyte.[19] (According to Smoluchowski's equation, the " viscosity " of a suspension is a function of the square of the electrokinetic potential of the particles.) Mattson considered the hydration

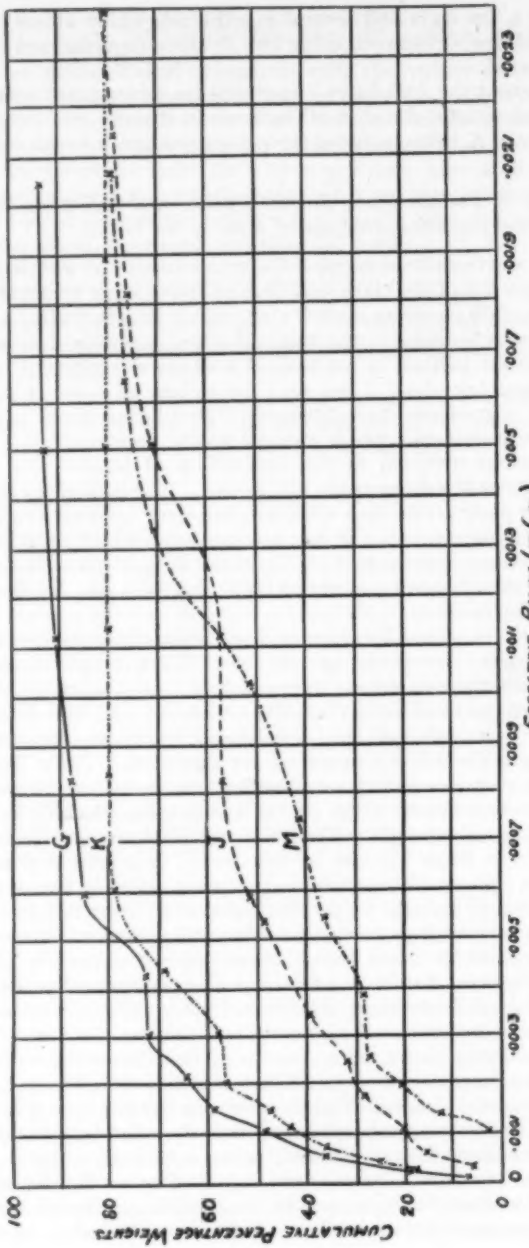

FIG. 6.

G—alluvial clay *G*; *K*—clay *K*; *J*—blue shale *J*; *M*—mottled clay *M*.

of the clay to increase with the exchange capacity—*i.e.*, with the ratio of silica to sesquioxides.

It will be apparent that these statements concerning the effects of silica–sesquioxide ratios require some qualification, particularly with regard to particle sizes.

In a few cases the fraction of a clay having a falling velocity of less than 1 mm./sec. at about 18° C. was separated by elutriation and sent for analysis under Dr. H. F. Harwood. However, three fractions embracing the whole of the London clay were analysed, and the silica–sesquioxide ratio was found to be highest in the coarsest fraction—a result to be expected, since most quartz was likely to be present in it. Yet it was equally clear that the finest fraction gave the most viscous suspensions. On the other hand, practically the whole of the Stockolite and the Aquagel was finer than 200-mesh I.M.M. (the actual size distribution was not determined). Stockolite is a high-grade china-clay, and analyses of typical china-clays give the silica–sesquioxide ratio as 1·13 to 1·22. Data in the Aquagel pamphlet put the ratio for that material at 2·26, and undoubtedly Aquagel formed the more viscous supensions.

In Table III are listed a number of the properties of four of the clays analysed. It is not possible to give relative values to some of the properties, and the clays can merely be placed in order in these respects.

TABLE III.

	Alluvial clay *G.*	Clay *K.*	Mottled clay *M.*	Blue shale *J.*
Decreasing order of "viscosity"-producing power . . .	4	3	2	1
Decreasing order of stress intercept-producing power . . .	1	3	4	2
Relative values of estimated total surface per gram of clay . .	6·7	6·3	1·0	2·8
Silica–sesquioxide ratio of fine fraction separated by elutriation .	1·89	2·99	2·82	2·42

The results of analyses put five clays in order of their "viscosity"-producing power, but a sixth was a marked exception. Furthermore, when the relative values of the estimated total surface per gram were considered, three clays fell in the order of their "viscosity"-producing power, whilst the fourth was outstanding. It seems, therefore, that many factors may have to be taken into account in order to predict the "viscosity"-producing power of a clay.

II. THE CONCENTRIC CYLINDER ROTATING VISCOMETER.

Ambrose and Loomis [20] used a concentric cylinder viscometer to examine a 5 per cent. bentonite suspension. Briefly, their conclusions were as follows: On a curve where torque was plotted against the rate of revolution, they found that when measurements were made at successively higher

speeds, and then at speeds which decreased in steps, the former curve lay above the latter. In some cases the torque increased for a time at a constant rate of revolution. "A substantially constant deflection could be attained by subjecting the fluid to a constant angular velocity for thirty minutes up to several hours." The time necessary to break down the gel to equilibrium between angular velocity and shearing stress was shorter than the period of reformation of a gel which had been subjected to a high rate of shear. A 16 per cent. change in torque occurred in 50 minutes at a speed of 3·68 r.p.s.

Through the kind offices of Mr. L. G. Gabriel, it was possible to borrow a Hatschek concentric cylinder viscometer from Messrs. Colas Products, Ltd., but difficulties soon appeared in using it for the examination of clay suspensions. It was not feasible to fill it through the tap, as advised; air was apt to be trapped and the suspended cylinder displaced with the more viscous suspensions, and in the absence of a constant temperature chamber, temperature control was not very satisfactory. However, certain features of the suspensions were examined by using it.

Relaxation and Rigidity.

If the inner cylinder was twisted a little with the outer cylinder stationary, its deflection decreased with time, relatively quickly at first, and then more slowly, until it reached a value which, it seemed, could persist indefinitely unless the instrument was disturbed. The final value was not the zero observed on suspending the inner cylinder, showing that some muds are capable of supporting a measurable stress. Richardson,[21] and McDowell and Usher [22] have made similar observations. Their findings—(*a*) that the critical stresses were difficult to determine accurately,[21] and (*b*) that if the apparatus was disturbed the deflection dropped suddenly, but not necessarily to zero, and the relaxation curve (deflection plotted against time) continued parallel to the direction it was following before the disturbance [22] —were borne out. Thus, the instrument can be employed for the rough comparison of critical shearing stresses or "yield values."

Lag, Breakdown, Thixotropic Recovery, etc.

Various apparently anomalous results arose from the protracted lag of the suspended cylinder in taking up the deflection appropriate to the rate of rotation of the outer cylinder and the instantaneous "viscosity," and the position was further complicated at times by the suspended cylinder sticking and giving a fictitious instead of a true value for thixotropic equilibrium.

Increased Sedimentation under Shear.

On emptying the concentric cylinder viscometer, at times the suspicion arose that the material at the bottom was especially concentrated, even with seemingly stable muds, and samples taken after shearing one mud for 4 hours gave clay concentrations of 38·2 per cent. and 42·87 per cent. at the bottoms of the inner and outer cylinders, respectively. Theoretical considerations indicated that shearing was likely to increase sedimentation in these muds.

In order to investigate the matter further, a simple viscometer was constructed, consisting of two concentric glass cylinders, the inner one not quite reaching to the bottom of the outer one and being capable of rotation. A known weight of 80–120-mesh (I.M.M.) sand was added to a 4·19 per cent. Aquagel suspension and shaken well. Some of the mixture was poured into the viscometer, and a like quantity of the mixture was poured into a twin apparatus, the inner cylinder of which was not, however, rotated. When the material in the first instrument had been sheared for 40 minutes at 3·69 r.p.s., the material between the two cylinders was removed in each case, and afterwards that within the outer cylinder but below the inner cylinder was also removed. The percentage of sand in each of the four samples was determined.

TABLE IV.

	Percentage of sand.	
	Sheared sample.	Unsheared sample.
Upper portion between the cylinders . .	3·55%	7·70%
Lower portion below the inner cylinder .	14·95%	6·10%

In a second experiment crushed oil shale (80–120-mesh I.M.M.) was added to the Aquagel which was put in the viscometer. The dark colour of the shale rendered the movements of the particles very clear. Again a twin sample was set up, but not subjected to shearing. In the unsheared sample there were no signs of sinking of the shale particles; merely a little water separation on the surface of the Aquagel. In the sheared sample, at low rates of rotation of the inner cylinder, the shale particles sank along spiral paths and accumulated just below the bottom of the inner cylinder —*i.e.*, just below the zone of shearing. No change was seen in the material well below the inner cylinder. On raising the rate of rotation of the inner cylinder, a speed was attained above which a new phenomenon appeared. A series of parallel bands was observed in the suspension, towards the edges of which shale particles could be seen moving quickly upwards and downwards from the middle of the bands. These bands seemed to sink slowly down the cylinder, but were ever replaced by fresh bands at the top. No accumulation of oil shale was evident in the region below the inner cylinder. Undoubtedly this was a turbulent condition under which the particles did not sediment, whereas under stream-line conditions, which must be realized for ordinary viscometric measurements, sedimentation took place.

According to Barr,[23] Taylor has examined the general case of concentric cylinder viscometers in which both cylinders rotate in the same or opposite directions, and has obtained a formula which reduces to :—

$$\frac{\Omega_c^2 a^2 d^2}{\frac{1}{2}(a+b)v^2} = \frac{\pi^4 f}{0{\cdot}0571 f^2 + 0{\cdot}00056}$$

for the case where only the inner cylinder rotates. Ω_c is the critical speed of rotation of the inner cylinder for turbulence; v is the kinematic vis-

cosity; a is the radius of the inner cylinder; b is the radius of the outer cylinder; $d = b - a$; $f = 1 - \frac{0{\cdot}652d}{a}$. The formula assumes that $\frac{d}{a}$ is small, but Lewis found critical speeds in excellent agreement with it up to $\frac{d}{a} = 0{\cdot}71$. Accurate centring and mounting of the cylinders is essential, and their lengths should be many times their diameters. When instability arises, it is three-dimensional, outward radial flow occurring at intervals of approximately $2d$ along the cylinders. This was about the width of the bands observed here.

One very viscous clay suspension failed to give any signs of separation, although turbulence was not apparent, but a second showed sedimentation, as is proved by the following data :—

TABLE V.

Time of shearing or standing: 4 hr.

Rate of revolution of inner cylinder in sheared sample: 2·3 r.p.s.

	Concentration.	
	Sheared sample.	Unsheared sample.
Upper portion between the cylinders . .	32·10%	38·57%
Lower portion below the inner cylinder .	50·54%	40·63%

Thus, although a concentric cylinder viscometer of the Hatschek type would, at first sight, seem superior to capillary instruments, since thixotropic equilibrium could be attained, in practice, in examining thick heterogeneous clay suspensions, many difficulties arise. Lag, induced sedimentation, and the length of time needed for a fair definition of the torque-rate of shear curve are among these, and its main value would therefore appear to be for demonstrating the presence of thixotropy.

III. DETERMINATION OF "YIELD VALUES."

The intercept on the stress axis obtained by extrapolation of the part of the flow-curve representing essentially stream-line flow is a function of the yield value as used in the Buckingham equation, being $\frac{4}{3}$ of that quantity. In a drilling mud the yield value is an extremely important property. Its direct measurement, and the investigation of its changes with time and other factors in thixotropic muds, are matters of no little consequence. To examine these points seems rather beyond the scope of the procedure used in the ordinary derivation of the stress intercept.

A number of workers have paid some attention to the direct measurement of yield values, but it is not improbable that the factor examined in some instances was not exactly that involved in the Buckingham equation, nor was it simply related to it. Meyer [24] used a thin plate which was allowed to fall edgewise in the mud. Investigation showed that this apparently simple method is fraught with many practical difficulties, and

this is supported by the detailed work of Evans and Reid.[25] The disturbance of the mud by the falling plate is one undesirable feature. Evans and Reid's modification of the idea is an improvement.[25] A method which is capable of greater accuracy employs the twisting of the upper end of a wire carrying a cylinder or vanes suspended vertically in the material under test. This type of apparatus has been used by Schwedoff,[26] Hatschek and Jane,[27] McDowell and Usher,[28] Richardson,[29] Evans and Reid,[25] Russell[30] and others. Some measured the angle through which the torsion head could be turned before the suspended system began to twist; others moved the torsion head through a large angle and recorded the behaviour of the suspended system; a third group made observations which were a combination of the two preceding methods.

In the present work both cylinders and vanes have been used. They were made of brass, and the overall dimensions of the vanes were almost the same as those of the cylinders. The cylinders or vanes were suspended centrally in a standard beaker containing the mud under test, and were immersed to a fixed point on the thin spindle connecting them to the supporting torsion wire.

Cylinder :	Length of cylinder	5·192 cm.
	Diameter of cylinder	1·577 cm.
	Length of spindle	2·575 cm.
	Diameter of spindle	0·409 cm.
	Length of spindle immersed	1·180 cm.
Vanes :	Length of vanes	5·164 cm.
	Diameter of enveloping surface	1·569 cm.
	Length of spindle	2·591 cm.
	Diameter of spindle	0·406 cm.
	Length of spindle immersed	1·196 cm.
	Diameter of expansion carrying the vanes	0·900 cm.
	Length of expansion carrying the vanes	4·700 cm.
	Thickness of the vanes	0·051 cm.

Six vanes were spaced equally around the circumference of the expansion, and they projected equal distances at the two ends of the latter.

Container :	Mean diameter of beaker	6·77 cm.
	Depth of filling	6·87 cm.
Torsion wire :	Length of torsion wire	40·95 cm.
	Diameter of torsion wire	0·0274 cm.

To twist one end of the wire through an angle of one radian when the other end was fixed needed a couple of 422 cm.-dynes.

The torsion head was twisted at a slow uniform rate (1° per second, unless otherwise stated) by an electric motor working through a reduction gear. The positions of the torsion head and the suspended system were shown by pointers moving over circular scales. Since the torsion head rotated at a uniform rate, it was usual to read the position of the suspended system for every 10° of rotation of the former. The twist (angular difference of rotation of the top and bottom of the torsion wire) was plotted against the total rotation of the torsion head. Such observations were supplemented by noting the angle at which the suspended system began to turn rapidly. Otherwise the maximum twist deduced could be in error by almost 10°.

On account of muds not being true liquids, in pouring a mud into the

beaker it was necessary to prevent the suspended system from being carried out of centre. Hence stops were provided to hold the pointer and the suspended system in zero and central positions respectively, and the mud was introduced through a T-connection with outlets on opposite sides of the suspended system to assist in its uniform distribution.

Since the properties of a mud are a function of the mechanical treatment and the time of standing, the need for careful control of these factors in order to get consistent results cannot be too strongly stressed. Indeed, it would seem that to get the best results and to handle very thixotropic and highly viscous muds, a rather elaborate filling apparatus is desirable. Perhaps a piston which could be moved at a fixed rate to drive the mud through a fine screen (to give a uniform breakdown), and thence via a forked tube, such as is employed for dividing samples in agricultural laboratories, would meet the case.

From the nature of the measurements, it might be expected that the stress at which a cylinder begins to turn (or the plate ceases to move in the shearometers) is likely to show affinities with the point A at which plug-flow began in Scott Blair and Crowther's flow-curves. When Scott Blair made this suggestion,[31] Evans could offer no evidence to show whether it measured A or the yield value, but observed that the results were slightly less than would be expected from measurements of the yield value made by other methods. The published data show A to be much less than the yield value, and it is recorded that A is at the same point whether approached from higher or lower stresses. This seems to imply that A is independent of the time factor. Ordinarily the results obtained by twisting a cylinder will not escape the inclusion of time effects.

How far the value of A depends on the nature of the solid surface is uncertain, but it has been shown to be dependent on the condition of the surface.[33] Russell [30] used a vane to eliminate "the possibility of slipping," and it seems likely that the vanes measure a property more nearly comparable to the yield value than does a cylinder.

When the bob (*bob* will be used in speaking generally of the cylinder and vanes) is immersed up to a point on the spindle, two modes of yield at its upper end seem possible, these depending on the depth of immersion and the material under test, (*a*) yield along the surface of the upper end of the bob and the surface of the spindle; (*b*) yield along a cylindrical surface continuous with the surface of the enveloping cylinder, if the force necessary would be less than that required to cause yield as in (*a*).

The systematic examination of a series of clays has not yet been undertaken. Therefore the following results are merely intended to give some idea of the behaviour of clay suspensions in the instrument.

Elasticity, Relaxation and the Yield Point.

The first point of note is that as the torque was increased, and before the yield took place, the suspended system showed a small rotation which was roughly proportional to the torque. Undoubtedly this was due to elasticity in the mud. For the cylinder this elastic yield was usually about 3° per 100° of torque, and for the six-vaned bob approximately twice that amount was common. Near the yield point the elastic yield increased at

an increasing rate. If the rotation of the torsion head was stopped before the yield point was reached, a limited relaxation occurred.

When the yield took place, the deflection fell. This fall was more rapid for the cylinder than for the vanes, and usually faster the higher the yield value and the more thixotropic the mud. In the case of the cylinder, when it had been dried and allowed to stand over-night, the yield point with a given mud was much higher than when it was dried and used again within a few minutes. Consequently, for consistency the cylinder was given a preliminary mud-wetting and drying before use. The vanes gave the same value whether dried over-night or wetted and dried immediately before use.

In general, with both the vanes and the cylinder the yield point was higher the longer the mud had stood in the beaker. Thus for one mud the times at which the experiment was commenced after starting to introduce the mud into the beaker were 212 sec., 332 sec., 600 sec., and 1800 sec., and the corresponding yield points with the cylinder were 168·5°, 169·5°, 179·0°, and 196·5°, respectively.

An instance was noted where the yield point decreased with increased time of standing. This may have been due to instability of the mud.

Since the cylinder when dried over-night gave a high yield point, it was decided to examine the effect of a relatively thick surface water-film. Both the cylinder and vanes were used, first wetted followed by drying in the standard manner, and then when dipped in water and not dried. The results, as was to be expected, showed that the presence of a relatively thick water film reduced the yield point with the cylinder (a 7 per cent. reduction was noted), but it seemed that the water had little or no effect in the case of the vanes. The indication is that the yield with the latter is not at the main surfaces of the vanes.

A further test was made in which a thick water film was produced electrically at the surface of the bob while it was in the mud under a torque equal to about one half of the yield point expected under normal conditions. The beaker containing the mud was lined with tinfoil and connected to the positive pole of a direct-current supply. The bob was connected to the negative pole (not via the torsion wire). The torsion head was set rotating, and on reaching a torque which was slightly less than half the yield point, the current was switched on. This set up electrophoresis,[24] and the water moved towards the negative pole, the clay towards the positive pole. Thus water accumulated around the bob. In two sets of experiments with the cylinder the following results were obtained :—

1(*a*) Normal yield point at 63·5°. Applied a torque of 31·5°, and then switched on a current of 0·6 amp. The torque fell almost immediately to 3·4°.

1(*b*) Normal yield point at 71·0°. Applied a torque of 35·5°, and then switched on a current of 1·0 amp. for a few seconds. The torque fell to zero.

In the case of the vanes the results were quite different :—

2(*a*) Normal yield point at 119·5°. Applied a torque of 51·0°, and switched on a current of 0·5 amp. for 50 sec. The torque fell only to 47°.

2(*b*) Normal yield point at 115·5°. Applied a torque of 51·0°, and switched on a current of 0·6 amp. for at least 20 sec. The torque fell only to 48·3°.

When the rotation of the torsion head was continued in 1(*a*) after applying the current, a yield occurred at 13°; in 2(*a*) continued rotation caused a yield at 157°. In the former experiment the time of the second yield was 1508 sec. (300 sec. after applying the current), in the latter 1430 sec. (280 sec. after applying the current).

The reproducibility of the yield point was not so good with the cylinder as with the vanes. Occasionally the cylinder gave results which differed by 15 per cent.

Using the same cylinder and vanes, tests were carried out to find the effect of varying the diameter of the mud container. The depth of filling was kept constant.

TABLE VI.

14·77% Clay *N*.

Diameter of container.	CYLINDER.			VANES.		
	Container filled in:	Started expt. at:	Yield point.	Container filled in:	Started expt. at:	Yield point.
6·77 cm.	56 sec.	600 secc.	72·0°	60 sec.	600 sec.	95·5°
4·05 „	25 „	600 „	100·0°	65 „	600 „	119·5°
3·05 „	40 „	600 „	104·0°	50 „	600 „	123·5°
6·77 „	53 „	900 „	73·5°	60 „	900 „	101·0°
4·05 „	41 „	900 „	108·5°	50 „	900 „	124·5°
3·05 „	47 „	900 „	103·5°	30 „	900 „	117·0°

In a narrow container the application of a given torque would set up a bigger strain than in a wide container. Hence yield might be expected to occur at a lower value. The fact that it did not do so is to be interpreted as showing that the strength of the gel-structure built up was greater in the narrow than in the wide container. The opposition of these two effects is perhaps indicated by the fact that on standing for 900 sec. the yield was slightly lower in the narrow than in the medium container.

Gross eccentricity of the bob gave a slightly higher yield point than the normal position.

Examination of the effect of the rate of rotation of the torsion head on the yield point, the observation being commenced at the same time in each case, showed a small decrease in the yield point with increased rate of rotation for the cylinder with one mud, but the results were inconclusive with a second mud and when the vanes were used. A slight decrease might be expected, since the torque increases more quickly under the higher speeds of rotation, and therefore a given torque will be attained earlier. On the other hand, if, when movement of the bob begins, it is very slow, then the tendency of the torque to increase due to the continued rotation of the torsion head may exceed the tendency towards its reduction resulting from the movement of the bob relatively to the mud. Such movement

was always slower with the vanes than with the cylinder, and hence may partly explain the inconsistencies.

Although no systematic investigation of different clays has been undertaken, it is clear that the yield points vary widely for the different muds, and they increase very quickly as the concentration increases. This holds for both the cylinder and the vanes.

TABLE VII.

Cylinder: mud-wetted and dried immediately before each observation.

Material.	Beaker filled in:	Started expt. at:	Temperature, ° C.	Yield point.
41·13% Blue shale *I*	50 sec.	600 sec.	19·1	23·0°
51·79% " "	70 "	600 "	19·0	35·5°
34·04% Mottled clay *M*	60 "	600 "	22·0	12·0°
45·92% " "	1040 "	1200 "	23·7	158·5°
14·77% Clay *N*	56 "	600 "	16·3	72·0°
18·18% "	130 "	600 "	16·0	179·0°
29·15% Unweathered London clay	70 "	600 "	20·2	61·0°
20% Stockolite with 2·925% of Aquagel	60 "	600 "	17·4	10·0°
*5·36% Aquagel	400 "	600 "		256·0°

* (The cylinder was not given a preliminary mud-wetting and drying for this observation.)

TABLE VIII.

Vanes: Mud-wetted and dried immediately before each observation.

Material.	Beaker filled in:	Started expt. at:	Temperature, ° C.	Yield point.
14·77% clay *N*	55 sec.	300 sec.	18·0	109·5°
16·68% "	50 "	300 "	17·9	192·0°
28·49% clay *Q*	75 "	300 "	17·9	193·0°

For all the muds examined, the yield point with the vanes was higher than with the cylinder. The ratio of the yield point for the vanes to that for the cylinder apparently varied with the concentration of the clay suspension, for at 900 sec. it was 1·37 for a 14·77 per cent. clay *N* suspension, and 1·74 for a 20·35 per cent. clay *N* suspension, and at 600 sec. for the former suspension it was 1·33.

The Effect of Varying the Number of Vanes.

The standard vaned bob had six vanes. Russell [30] used a glass vane 1·5 cm. square. Therefore the question arose as to whether the number of vanes affected the results. A set of vaned-bobs was obtained which were of approximately the same over-all dimensions and differed only in the number of vanes—two, four, and eight. When used under similar conditions with several suspensions the least yield value was obtained with two vanes and the greatest with four vanes. The ascending part of the curves of torque against the angle turned through by the torsion head for the four- and eight-vaned bobs coincided almost to the yield point of the latter, but the two-vaned bob showed a larger elastic yield and a less sharp break.

Nature of the Curves beyond the Yield Point.

The ascending part of the curves and the yield point are not the only features of interest. The nature of the curves beyond the yield point also seems of importance, and has revealed at least one significant feature. Evans and Reid [25] noted that to obtain consistent values for the yield point was rather difficult. They used a cylinder and applied the torque by twisting the torsion head in steps of 5°. Presumably this was done at equal time intervals. After the yield they found that the torque fell rapidly to an almost constant value. (Their curve shows a slight fall as the total twist increases.) This value, θ_2, they found to be more consistent, and state that it should be about the true yield value. Their experiments gave slightly lower figures. One reason for this will become apparent shortly.

In the present apparatus, as a result of the continuous rotation of the torsion head, the extreme slowness of the initial motion when yield takes place, and the inertia of the suspended system, the torque may attain a value slightly in excess of the yield point. There is little doubt that this accounts, at least partly, for the descending part of the curve being steeper with the cylinder than with the vanes, and the break being sharper with the former. Also, due to its relatively high moment of inertia, the cylinder may swing to a position slightly beyond that at which the torque and rigidity of the mud would be in equilibrium. It is on this account that when an accidentally high yield point is recorded the break is sharper, and the suspended system swings to a lower value than usual. Hence a reciprocal relationship between θ_1 (the yield point) and the value of θ_2 immediately after the yield is to be expected, although the variations in θ_2 will not necessarily be so large as those in θ_1.

The present set-up is comparable to a concentric cylinder viscometer, employing very low rates of shear.* Consequently when equilibrium is reached the torque will be proportional to the "viscosity" at these low rates of shear. Indeed, in testing the apparatus with very viscous liquids, proportionality between torque and viscosity and between torque and rate of rotation was found to obtain approximately.

In using the cylinder with muds, two quite different types of curves were obtained. In the first, the curve, after the rapid fall following the yield, remained horizontal or declined a little to a steady value (Fig. 7). When the latter was reached, equilibrium existed between the rate of shear, the torque and the thixotropic condition. In a few instances the curve rose slightly to a steady value, due to the cylinder having swung too far.

The effect of different speeds on the final steady value is somewhat problematical. With a true liquid the torque at equilibrium will be proportional to the rate of rotation, in the absence of turbulence. However, with a thixotropic material an increased rate of rotation increases the thixotropic breakdown, thereby reducing the "viscosity." Hence, whether increasing the rate of rotation increases or decreases the final steady deflection depends on whether the tendency to increase the torque resulting from the higher speed is greater or less than the "viscosity" reduction

* When the cylinder is moving relatively to the mud or other fluid, the torque and rate of rotation are balanced against a "viscosity" factor; when the cylinder is stationary, the torque is balanced against a rigidity factor.

due to thixotropic breakdown.* For similar reasons the effect of changing the diameter of the container whilst the speed was kept constant gave equally unpredictable results. These remarks are also applicable to the vanes.

In the case of a Stockolite–Aquagel suspension which was examined at intervals of several hours or of a day and more, the position of the almost horizontal parts of the curves rose with the time of standing, but the observations were not continued for a sufficient length of time to determine if ultimately they would all attain the same value. There were signs that such would be the case.

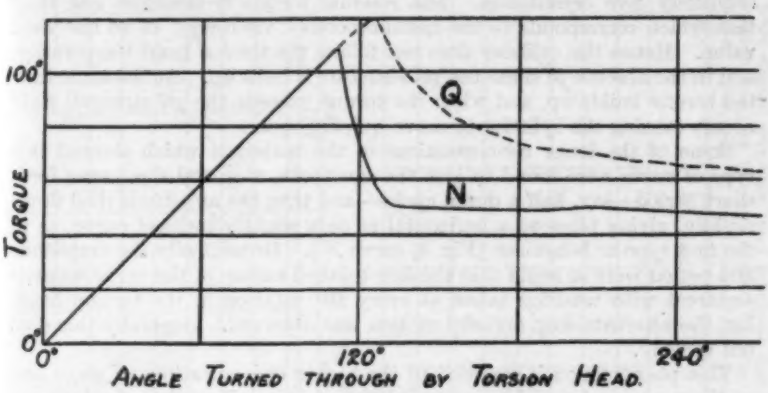

FIG. 7.

Cylinder mud-wetted and dried immediately before use; rate of rotation of torsion head—360° in 204 sec.; standard beaker as container.

Q—28·49% clay *Q*; beaker filled in 60 sec.; observation commenced at 300 sec.; temperature 17·8° C.

N—16·68% clay *N*; beaker filled in 55 sec.; observation commenced at 300 sec.; temperature 18·0° C.

The second type of curve was a little unexpected, and was shown by the more thixotropic muds. Some of Russell's results [30] seem to indicate a similar phenomenon. In this type of curve, at the end of the swing after the yield the cylinder remained stationary for a period, with the result that the torque built up. This continued until a second yield occurred (there was a slight elastic yield as before the initial yield), and then the cylinder turned rapidly. It halted again, and the cycle was repeated. The result was a saw-toothed curve with asymmetrical teeth (Fig. 8 curve *N*). It must be noted that the values at which these secondary yields took place were much less than that of the initial yield. Often there were a few

* The exact nature of the yield with the cylinder has not been determined. If it is the same as point A on Scott Blair and Crowther's flow-curves, then the subsequent motion, provided it is not too rapid, will probably be a slip involving only a thin surface (water) film. However, when the rate of rotation exceeds a certain value, relative motion will occur between adjacent thin annuli of mud. The fact that the yield value increased when the diameter of the container was reduced, seems to show that if it is a question of the rupture of forces across a thin surface film, those forces are not independent of the conditions existing within the surrounding mass of mud.

irregularities in the curve before it settled down to the consistent saw-toothed form. After this phase there was a steady decrease in the values of the maxima and in the amplitude, although there were instances in which the maxima rose a little and the amplitude increased at first. Some of the more thixotropic muds persisted in this form of curve as far as the experiment was taken, the decline in the maxima and the diminution in amplitude both becoming smaller.

Obviously the cause of this behaviour lies in the alternate building up and breaking down of gel structure.* The momentum gained by the cylinder after a yield carries it a little beyond the point which would ordinarily give equilibrium. The residual torque is therefore less than that which corresponds to the instantaneous "viscosity" or to the yield value. Hence the cylinder does not follow the torsion head temporarily, and in the absence of shear the gel structure is built up. At the same time the torque builds up, and when the torque exceeds the gel strength yield occurs causing the cylinder to move quickly again.

Some of the lower concentrations of the materials which showed this type of curve were found to give the saw-tooth, stop-and-slip, curve for a short period—say, half a dozen cycles—and then the amplitude died down rapidly, giving place to a horizontal or only slightly inclined curve, as in the first type of behaviour (Fig. 8, curve N'). Occasionally the amplitude and period were so small that the saw-toothed nature of the curve was not apparent with readings taken at every 10° rotation of the torsion head, but the alternate stop-and-slip motion was observed. Generally this died out quickly.

This phenomenon is confined to the higher concentrations of clays and to those suspensions which are most thixotropic. Rapidity of gelation is essential, for although the Stockolite–Aquagel suspension set slowly to a very strong gel, it did not give a saw-toothed curve for rotation at 1°/sec. The occurrence of the stop-and-slip curve is also a function of the rate of rotation of the torsion head. Materials which showed it at low speeds might give the curves in which it died out, at intermediate speeds, and fail to exhibit it at high speeds, merely giving curves of the first type. (By high speeds a few degrees per second is implied.)

A possible third type of behaviour was noted with a 45·92 per cent. suspension of mottled clay M (Fig. 8, curve M). This was a very viscous mud. Here the cylinder did not stop, but moved for a time at an almost uniform rate more slowly than the torsion head. This phase was ended by the occurrence of a yield, followed by the cylinder moving more quickly than the torsion head, stopping momentarily, and then repeating the cycle.

The vanes showed but one type of behaviour. After the yield the torque fell rapidly for a short time and then more gently, or gently all the

* Whether or not we assume that the initial and secondary yields occur in a mechanically similar manner, and that the yields are in any way comparable with A on Scott Blair and Crowther's flow-curves, it is clear that they are affected by thixotropy or some such phenomenon. The term "gel structure" has been used here, but it must be understood to imply the rigid forces across the thin water film postulated by Scott Blair and Crowther as the most likely explanation of A, if the yield with the cylinder is of the same nature as A, and/or the general gel structure of the mud mass if the yield disrupts the structure of the mud mass, and if the rate of rotation of the cylinder is sufficiently rapid to cause relative movement of the adjacent annuli of the main mud mass.

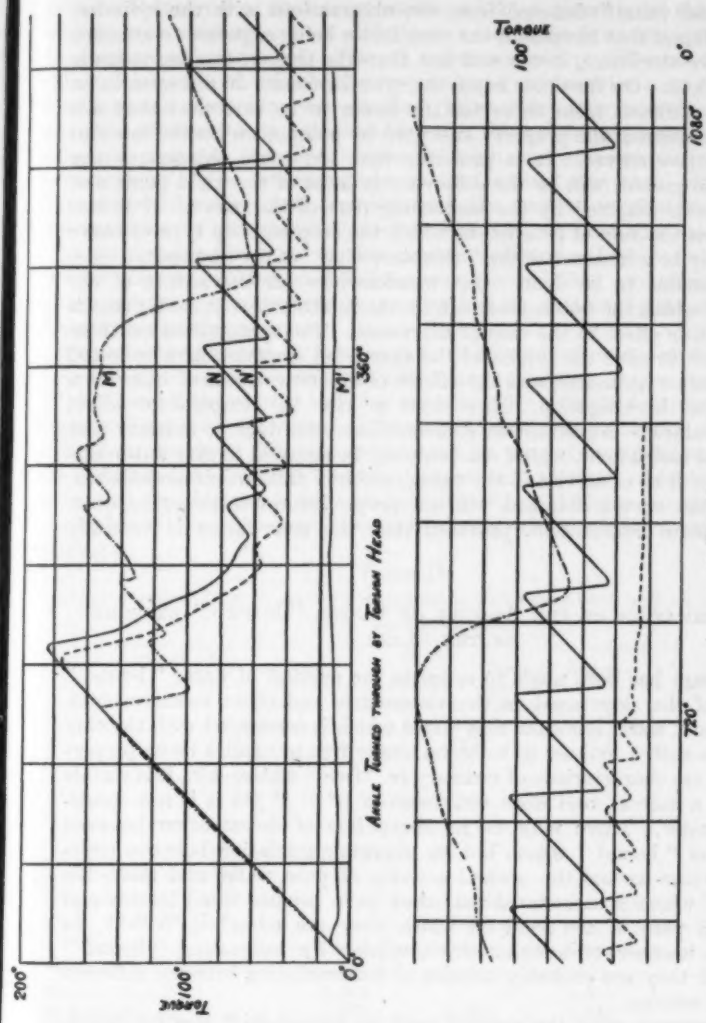

FIG. 8.

Cylinder mud-wetted and dried immediately before use; standard beaker; rate of rotation of torsion head—360° in 360 sec. Curve *M*—45·92% mottled clay *M*; beaker filled in 1040 sec.; measurement begun at 1200 sec.; temperature 23·7° C. Curve *N*—18·18% clay *N*; beaker filled in 65 sec.; measurements began at 900 sec.; temperature 17·3° C.; the saw-toothed curve persisted even after the torsion head had turned through 2520°; the mean level of the teeth had fallen slightly, and their amplitude had decreased gradually to 64% of the maximum value. Curve *N'*—17·87% clay *N*; beaker filled in 55 sec.; measurements begun at 600 sec.; temperature 19·5° C. Curve *M'*—34·04% mottled clay *M*; beaker filled in 60 sec.; measurements begun at 600 sec.; temperature 22·0° C.

time, until it came to an essentially constant value. Sufficient work has not been done to be absolutely certain, but it appears that the ultimate positions reached by the curves may be almost the same for the cylinder and the vanes (the overall dimensions of the bobs and other conditions being the same, of course), with the latter possibly a little the higher. The final level is much slower of attainment with the vanes.

For a few muds the yield value derived from the stress intercept of capillary-tube viscometric measurements has been compared with the

initial "yield value" deduced from the observations with the cylinder, but it was found that in spite of the time factor being expected to enhance the value for the latter, it was still less than the former, tending towards one half or less. On the other hand, the cylinder results do not seem to be sufficiently different from those for the vanes to be sure that they are merely a measure of the property indicated by point *A* on Scott Blair and Crowther's flow-curves. It is probable that the more thixotropic the material the greater will be the difference in level of the yield point and the final value attained by the succeeding part of the curve. It is also possible that the rate of rotation at which the stop-and-slip type of curve appears may be a measure of the "thixotropicity" of the suspension.

Much remains to be done. One wonders how far the nature of the material of which the bob is made affects the results; it is probable that it will have little effect in the case of the vanes. The speculations on those points which involve the inertia of the suspended system might be tested by using hollow cylinders, and the effects of different depths of immersion also require investigation. How does a rise in temperature affect the yield values? Nevertheless, sufficient has been done to indicate that this type of instrument, which can probably be adapted to give automatic recording, will be of service in the examination of thixotropic suspensions, and that the curves obtained will, on proper interpretation, give quite a lot of useful information, provided that the time factor is carefully controlled.

IV. Estimation of the Amount of Water "Bound" by some of the Clays.

An attempt has been made to estimate the amount of water "bound" by some of the clays used in the viscometric and other measurements. By "bound" water is meant that water which is associated with the clay particles in such a manner as to be no longer free to exhibit those properties which are characteristic of ordinary or "free" water—*e.g.*, it is unable to act as a solvent and does not freeze at 0° C.,[35] yet it is not constitutional water. There may be no sharp line of demarcation between "free" and "bound" water, but an insensible gradation between molecules of water having the normal activity of pure water and those the activity of which is so reduced that they have become to all intents and purposes a part of the solid on which they are adsorbed.[36, 37, 38] In general, a number of methods are available for estimating "bound" water, and they are probably capable of differentiating between different degrees of activity.

In the present work the method used by Dumanski[39] was employed, with sucrose as the "tracer." It has been assumed that the presence of the sucrose did not disturb the water equilibrium in the clay–water system, but no evidence is available regarding the validity of this assumption.

A known weight of a standard sucrose solution (containing about 25 per cent. by weight of sucrose) was placed in a weighed super-centrifuge tube, fitted with a celluloid cap to prevent evaporation losses. Finely ground clay was added, and the amount introduced was determined by weighing. A sample of the clay was heated to 110° C. to find the amount

of water driven off at that temperature, whilst a quantity of the sucrose solution was weighed and set aside to serve as a check on the strength of the sucrose solution used. Sets of tubes containing different clays or different amounts of a single clay were allowed to stand for a set time (for most a period of six days was adopted), after which they were centrifuged and then weighed to find the loss of water (if any) by evaporation. The refractive index of the clear sucrose solution was measured in an Abbé refractometer. The concentration of the sucrose was then obtainable from standard tables, and together with the various weighings and the concentration of the standard sucrose solution, enabled the amount of "bound" water per gram of clay to be calculated. Tests in which the ground clay was added to distilled water showed that any soluble salts which may have been present in the clay had no, or a negligible, effect on the refractive index of water.

The results obtained so far are not entirely satisfactory, nevertheless they are of considerable interest. It is probable that better agreement will be found if the sucrose and clay are stirred by a weighed stirrer kept in the centrifuge tube, for some of the clays (Aquagel in particular) are very difficult to disperse. Thus parts may not be properly wetted, leading to low values for the "bound" water. Experiment seems to show that four days, and possibly much less, are sufficient to yield the maximum value attainable without the more thorough mixing which will be achieved by stirring.

TABLE IX.

Approximately 3 gm. of Aquagel were used in each experiment, with 20 c.c. of "25%" sucrose solution.

Time of standing.	"Bound" water.
23 hr.	0·14 gm./gm. of clay.
94 ,,	0·28 ,, ,,
142 ,,	0·29 ,, ,,
213 ,,	0·15 ,, ,,
262 ,,	0·28 ,, ,,
310 ,,	0·27 ,, ,,

TABLE X.

	"Bound" water (gm./gm. of clay).			
	Using 5 gm. of clay.		Using 8 gm. of clay.	
Alluvial clay *R* . .	0·012		0·012	
Mottled clay *M* . .	0·039	0·127	0·066	
Blue shale *L* . . .	0·065		0·048	0·065
Alluvial clay *G* . .	0·080		0·057	0·105
Clay *K* . . .	0·053		0·053	
Blue shale *J* . . .	0·029		0·029	
Alluvial clay *H* . .	0·039	0·118	0·063	
Unweathered London clay	0·059		0·053	0·091
Shale *P* . . .	0·101		0·087	0·139
Clay *N* . . .	0·093		0·081	0·123

A value of 0·022 gm./gm. was obtained for Stockolite.

The facts that a measurable amount of water is bound by the clays, and that the highest value is associated with Aquagel and the lowest, with the exception of alluvial clay *R*, with Stockolite, seem significant. If this "bound" water can be partly or wholly sheared off or distorted under shear, it offers a possible partial explanation of the reduction in "viscosity" of these clay suspensions with increased rate of shear. Whilst the figures are suggestive, they require checking, and they are not of the magnitudes which would seem consistent with some of the properties of the clay suspensions. However, it may be that the sucrose disturbs the clay-water equilibrium, or only reveals the most tightly bound water.

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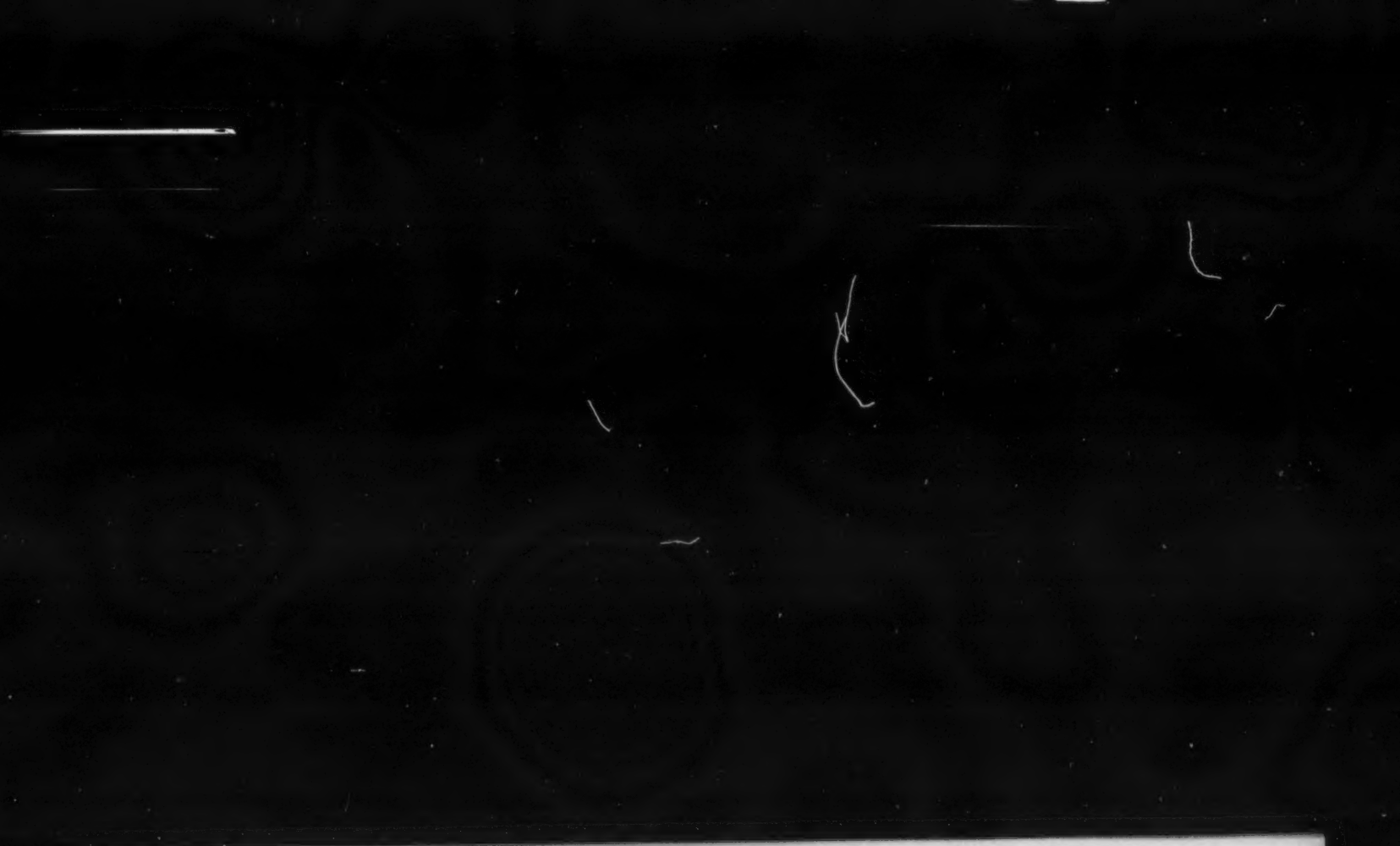
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